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Patentanmeldung Nr.

Patent application No. Demande de brevet nº

03257477.4

# PRIORITY

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention: (Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung. If no title is shown please refer to the description. Si aucun titre n'est indiqué se referer à la description.)

Thickener for paper coating compositions

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THE PATENT OF

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# STORING DIVI

## Thickener for Paper Coating Compositions

#### Technical Field

The present invention relates to paper coating compositions comprising a starch-based thickener, to paper products coated with such compositions and to methods of preparing such compositions and products.

#### Background of the Invention

Coating compositions have been developed that can contribute, amongst other things, to improved appearance and feel (e.g. improved gloss, slickness, brilliance, and colour), improved printability (e.g. smear-resistance, ink-absorption and adhesion) and improved strength. The ingredients included in such compositions can be divided into three main categories: pigments, binders and thickeners.

Thickeners, in particular, have to be chosen very carefully as they are responsible for determining the coating composition's rheological properties. It will have to be ensured, for example, that at low shear the coating composition has a low enough viscosity for easy pumping but a high enough viscosity to maintain a homogeneous suspension and to prevent excessive absorption into the paper. At high shear (for example during blade application of the composition), the viscosity will have to be low enough to ensure that an even coating of the composition can be applied over the entire surface of the paper without having to apply too high a blade pressure to obtain the desired coatweight. In addition, the coating composition should have good water retention values and torque properties and should be stable during storage and at the high temperatures required for drying. To meet all of these requirements, a number of different thickeners have been proposed.

To date, the most commonly used thickeners have included cellulose ethers such as carboxymethyl cellulose (CMC), modified starches and synthetic products such as water-soluble polymers. Unfortunately, none of these products have proved to be entirely satisfactory.

Cellulose esters suitable for use as thickeners tend to be obtainable only by relatively complex preparation methods. This is a disincentive in itself but also means that such products carry a prohibitively high price tag. Their use is further limited by their low solubility in water whereas it is desirable, in coating compositions, to have a high solid content. Finally, it has often been found that cellulose ester-based compositions do not have good stability (in terms of viscosity) at high shear or at high temperature.

Although some synthetic polymers have been developed to replace cellulose esters, these do not tend to have comparable thickening properties, for example in terms of water retention. They also have a lower capacity for optic brighteners whereas it is highly desirable to include such compounds in paper coating compositions.

Similarly, although some starch thickeners have been suggested (including, in particular, cold water, soluble starches obtained e.g. by roll drying of native or chemically modified starches), these do not provide the necessary viscosity to the coating compositions at typical thickener dosage levels, i.e. generally less than 2 parts per 100 parts pigment. Higher dosage levels of such starches becomes uneconomic and furthermore can impair desired properties of the final coated papers like e.g. gloss and mottling. Furthermore, at higher dosage levels, the starches would be referred to as co-binders rather than thickeners.

It is therefore apparent that there is a need in the art for coating compositions comprising improved thickeners. The present invention provides such compositions.

### Summary of the Invention

In a first aspect of the present invention, there is provided a paper coating composition comprising one or more thickeners, characterised in that at least one of said one or more thickeners is a cold water soluble starch ester, preferably a starch carbamate phosphate ester derived from potato or tapioca starch.

According to one embodiment, the composition will further comprise one or more pigments, one or more binders and, optionally, one or more additives. It can be

provided in dry or wet form. In its wet form, it should comprise 30-75% by weight dry substance.

According to a further aspect of the present invention, there is provided the use of a cold water soluble starch ester in the preparation of a paper coating composition.

According to another aspect of the invention, there is provided a process for the preparation of a paper coating composition comprising adding one or more pigments, one or more thickeners, one or more binders and, optionally, one or more additives to an aqueous solution and mixing, characterised in that at least one of said one or more thickeners is a cold water soluble starch ester. Preferably, the one or more binders are added to the aqueous solution before the one or more thickeners.

According to yet another aspect of the present invention, there is provided a method of manufacturing paper comprising applying to at least one surface of a sheet of paper or a paper web a composition as defined above or prepared according to the process described above. In one embodiment, the method will further comprise the steps of removing any excess coating composition, drying and, optionally, calendering the sheet of paper or paper web.

According to a yet further aspect of the present invention, there is provided a paper product coated with the above composition or manufactured according to the above method.

#### Description of the Figures

Figure 1 is a graphic representation of the Brookfield viscosity of a reference coating composition and of coating compositions comprising 0.2 parts CMC, 0.4 parts CMC, 0.6 parts CMC, 0.06 parts Noresin (a cold water soluble starch ester), 0.25 parts Noresin and 0.35 parts Noresin respectively.

Figure 2 is a graphic representation of the Haake viscosity of the above listed compositions.

Figure 3 is a graphic representation of the water retention values of the above listed compositions.

Figure 4 represents a comparison of the influence of CMC and Nozesin amounts on Brookfield viscosity.

Figure 5 represents a comparison of the influence of CMC and Noresin amounts on Haake viscosity.

Figure 6 represents a comparison of the influence of CMC and Noresin amounts on water retention values.

Figure 7 is a graphic representation of the Brookfield viscosity of compositions comprising the compositions produced in Example 2.

Figure 8 compares the Brookfield viscosity of fresh and stored compositions.

Figure 9 compares the Brookfield viscosity of fresh and stored compositions.

Figure 10 compares water retention values of fresh and stored compositions.

Figure 11 shows the influence of stirring time on Brookfield viscosity.

Figure 12 shows the influence of thickener type on torque.

Figure 13 shows the influence of thickener dry solid content on Brookfield viscosity.

Figure 14 compares the Bekk smoothness of paper coated with a CMC-based composition and paper coated with a Noresin-based composition (FS = felt side and WS = wire side).

Figure 15 compares the printing gloss of paper coated with a CMC-based composition and paper coated with a Noresin-based composition.

#### Detailed Description

The present invention provides a paper coating composition comprising one or more thickeners, characterised in that at least one of said one or more thickeners is a cold water soluble starch ester. Granules of cold water soluble starches swell in cold water (i.e. in water having a temperature of less than approximately 50°C) to give a viscous, colloidal dispersion. Thus, they are also known as cold water swellable or cold water swelling starches. Preferably, the starch ester of the present invention will be at least 90% cold water soluble.

In a preferred embodiment of the present invention, the starch ester will be a starch carbamate phosphate ester. It can be derived from any type of starch including, for example, potato, maize, wheat, rice, tapioca, sorghum and sago. Preferably, however, it will be derived from potato or tapioca starch.

According to one embodiment of the present invention, the starch ester will be prepared by heating a mix of starch, acid, urea, salt and water at low pressure. As noted above, the starch will preferably be potato or tapicca derived starch. The acid will ideally be an organic acid such as phosphoric or sulphuric acid and the salt will ideally be an alkaline salt such as ammonia or soda. For 100 parts starch, the initial mix should contain 0.02-100 parts each of acid, urea, salt and water. Preferably, for 100 parts starch, the mix will contain 2.5-40 parts of both acid and urea and 0.05-40 parts of both salt and water. Ideally, for 100 parts starch, the mix should contain approximately 10 parts of both acid and urea and approximately 5 parts of both salt and water. The mix should be heated for up to 24 hours at a temperature of 80-220°C. For best results, the mix should be heated for 2-5 hours at 120-160°C. The heating should preferably be carried out at a pressure between 0.001 and 0.8 bar. More preferably, it should be carried out at a pressure between 0.1 and 0.2 bar. Starch esters prepared in this way have been found to impart surprisingly good viscosity profiles when used as thickeners in paper coating compositions.

In particular, it has surprisingly been found that coating compositions comprising such thickener compounds have exceptionally good water retention values together with both high Brookfield viscosities (low shear) and low Haake viscosities (high shear). Advantageously, unlike with conventional thickeners, the viscosities of these

compositions are very stable, even after overnight storage.

Of course, the coating composition of the present invention may comprise more than one thickener. Thus, it may contain more than one type of cold water soluble starch ester or it may contain at least one cold water soluble starch ester in addition to one or more other thickener compounds. Thickener compounds include all compounds which, in solution, are capable of causing an increase in viscosity. Examples of such compounds include cellulose esters (such as CMC, hydroxyethyl cellulose, hydroxypropyl cellulose, ethylhydroxyethyl cellulose and methyl cellulose), alginates (such as sodium alginate), xanthan, guar, native or modified starches and synthetic polymers.

In any event, the one or more cold water soluble starch esters should account for 0.005-2%, preferably 0,008-1.7%, even more preferably about 0,01-1.5% of the dry weight of the coating composition of the present invention. It has indeed been found that, compared to conventional thickeners, much smaller amounts of cold water soluble starch ester are needed to achieve the necessary rheological properties for a good coating composition. As a result, the coating compositions of the present invention will be considerably cheaper to produce than those available at the time of this invention.

The coating compositions of the present invention should, of course, further comprise one or more pigments, one or more binders and, optionally, one or more additives. The pigments, binders and optional additive compounds can be selected amongst those available in the art and in accordance with the type of coating composition to be obtained.

Examples of pigments, both natural and synthetic, include: clays such as structured and calcined clays, hydrated aluminosilicates (such as kaolin clay), natural and synthetic calcium carbonate, calcium sulphate, silicas, precipitated silicas, titanium dioxide, alumina, aluminium tribydrate, plastic (polystyrene) pigments, satin white, tale, barium sulphate and zinc oxide. Preferably, the coating composition according to the present invention will comprise pigment in an amount of approximately 30 to

96%, preferably 45 to 96% by weight of the dry solids. Pigment content usually constitutes 4 to 20 times that of binder.

Examples of binders suitable for use in the composition of the present invention include: carbohydrate binders including starch binders (such as oxidised or esterified starch) and cellulose binders (such as CMC and hydroxyethyl cellulose), protein binders (such as casein, gelatine, soya protein and animal glues) and synthetic binders, especially latex binders (such as copolymer latexes, acrylic polymer latexes, vinyl polymer latexes) and synthetic resin binders. The coating composition of the present invention will preferably comprise 2-70%, even more preferably 4-30% by dry weight binder compounds.

Of course, the choice of pigment and/or binder and the amounts to be used will be determined in accordance with the desired properties of the coating composition being produced.

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The properties of the final coating composition can be further modified or enhanced by the use of optional additives. Examples of such additives include: surfactants (e.g. cationic surfactants, anionic surfactants, non-ionic surfactants and fluorinated surfactants), hardeners (e.g. active halogen compounds, vinylsulfone compounds, epoxy compounds, etc.), dispersing agents (e.g. polyacrylates, polyphosphates, polycarboxylates, etc.), flowability improvers, lubricants (e.g. calcium, ammonium and zinc stearate, wax or wax emulsions, alkyl ketene dimer, glycols, etc.), antifoamers (e.g. octyl alcohol, silicone-based antifoamers, etc.), releasing agents, foaming agents, penetrants, optical brighteners (e.g. fluorescent whiteners), preservatives (e.g. benzisothiazolone and isothiazolone compounds), biocides (e.g. metaborate, thiocyanate, sodium benzonate, etc.), yellowing inhibitors (e.g. sodium hydroxymethane sulfonate, sodium p-toluenesulfinate, etc.), ultraviolet absorbers (e.g. benzotriazole compounds having a hydroxy-dialkylphenyl group at the 2 position), autioxidants (e.g. sterically hindered phenol compounds), insolubilisers, antistatic agents, pH regulators (e.g. sodium hydroxide, sulfuric acid, hydrochloric acid, etc.), water-resisting agents (e.g. ketone resin, anionic latex, glyoxal, etc.), wet and/or dry strengthening agents (e.g. glyoxal based resins, oxidised polyethylenes, melamine resins, urea formaldehyde, etc.), gloss-ink holdout additives, grease and oil resistance

additives, levelling and evening aids (e.g. polyethylene emulsions, alcohol/ethylene oxide, etc.), etc.

The amount of each of these compounds to be added, if at all, will be determined in accordance with standard practice and with the desired properties of the coating composition to be produced in mind. The composition can be provided in dry form or in an aqueous solution. The aqueous solution should have a total content of 30-75% by weight dry substance. The remaining 25-70% will consist essentially of water and/or other suitable fluids such as solvents. If used, solvents will preferably be selected amongst organic solvents such as methanol. Ideally however, water alone will be used.

The paper coating composition in accordance with the present invention can be prepared simply by mixing the above ingredients (namely one or more pigments, one or more thickeners (at least one of which is a cold water soluble starch ester), one or more binders and, optionally, one or more additives) into the aqueous solution. Thus, the present invention further provides a process for the preparation of a paper coating composition and the use of a cold water soluble starch ester in such a process.

As pigments are generally the ingredient present in the largest amount, amounts of all other ingredients to be mixed into the aqueous solution can conveniently be expressed as parts per 100 parts pigment. Thus, for 100 parts pigment, 0.01-2, preferably 0,1-1 parts cold water soluble starch ester and 1 to 50, preferably 5 to 25 parts binder will be added to the aqueous solution. The ingredients can be mixed in any order or simultaneously. The cold water soluble starch ester can also be dissolved separately in water and added to the composition as a viscous solution. Preferably, the one or more cold water soluble starch esters (whether pre-dissolved or not) will be added to the composition after the one or more binders. The ingredients should be mixed for a sufficient time to form a substantially homogeneous slurry.

The coating composition thus prepared can either be stored or it can be applied directly to the paper. Thus, the present invention further provides a method of manufacturing paper products comprising applying to at least one surface of a sheet of paper or paper web a composition as defined herein.

The terms "paper" and "paper product" refer to sheet material of any thickness, including, for example, paper board, cardboard and corrugated board. The term "paper web", by contrast, refers to the continuous ribbon of paper, in its full width, at any stage during the paper making process.

Coating of the paper products can be carried out on the sheet forming machine or on a separate coating machine. Methods of applying coating compositions to paper products are well known in the art. They include, for example, air knife coating, rod coating, bar coating, wire bar coating, spray coating, brush coating, cast coating, flexible blade coating, gravure coating, jet applicator coating, extrusion coating, short dwell coating, slide hopper coating, curtain coating, flexographic coating, size-press coating, gate roll coating, reverse roll coating and transfer roll coating. According to the quality of paper desired, it can be coated only once or a plurality of times, provided that at least one of the coatings is in accordance with the present invention. If more than one coating is to be applied, both surfaces of the paper web can be coated.

After the coating step, excess coating composition can be removed. The paper is then dried and optionally calendered to improve surface smoothness and gloss and to reduce bulk. Drying methods include, but are not limited to, air or convection drying (e.g. linear tunnel drying, arc drying, air-loop drying, sine curve air float drying, etc.), contact or conduction drying and radiant energy drying (e.g. infrared or microwave drying). Calendering is achieved by passing the coated paper between calender mips or rollers (preferably elastomer coated nips or rollers) one or more times. For best results, calendering should be carried out at elevated temperatures. Ideally for each coating step, a dry coating weight in the range from about 4 to about 30g/m², preferably from about 6 to about 20g/m² will be achieved, with a coating thickness of 1-50µm.

Paper products coated with the above described composition or indeed obtained according to the above described method also form part of the present invention which will now be described in more detail by way of the following non-limiting examples.

#### Examples

Example 1 — Comparison of CMC and cold water soluble (cws) starch ester properties

A series of tests with 0.2, 0.4 and 0.6 parts CMC FF5 were performed and the amount of Noresin A 180 (a cold water soluble starch ester provided by Blattmann Cerestar AG) required to reach the same Brookfield viscosity was determined.

CMC and Noresin preparation:

CMC and Noresin were added to tap water at ~40°C and homogenised with a dissolver for 30 minutes. The CMC was prepared at 15% dry solids and the Noresin at 9.4% and 5.5% dry solids. Brookfield viscosity was then determined at 50°C.

Coating composition preparation:

The coating compositions were prepared as shown in Table 1.

Trials 1, 2, 3, 4 and 9:

For these compositions the CMC and the Noresin were added to the pigment slurry before the latex binder was added.

Trials 4a, 4b, 5, 6, 7, 8, 10, 11 and 12:

The latex binder was added first to the pigment slurry, then the Noresin was added.

For all trials, total dry solid content was adjusted to 69% by weight and the pH was set at 8.5.

The coating compositions were analysed according to standard industry methods with regard to Brookfield viscosity (low shear) and Haake viscosity (high shear). WRVs (water retention values) was measure using the Abo Akademi method.

CMC FF5 was used as a 15% dry solids solution. Lab trials showed that Noresin, at a 15% ds solution (4050 mPa.s at 50°C), is not comparable with CMC FF5. Even a 9.4% solution of Noresin reached a Brookfield viscosity of nearly 10000mPa.s and would therefore be too viscous to handle. Accordingly, the appropriate dry solid content of Noresin was determined to be 5-6% by weight (5,5% reached 3120 mPa.s at 50°C).

An evaluation of the coating compositions revealed that Noresin was much more effective than CMC at lower addition rates. It was indeed found that the addition of 0.5 parts CMC was comparable to the addition of only 0.09 parts of Noresin in a coating composition with 525mPa.s. To reach a coating colour of ~1400mPa.s only 0.35 parts Noresin were necessary compared to 0.6 parts of CMC. Accordingly, by using cold water soluble starches instead of CMC, significant cost reductions can be made.

Best results (i.e. more moderate thickening) were obtained with Noresin when it was added to the coating composition mix after the latex binder. Thickening is further reduced by adding any remaining water and fully homogenising the mixture.

The full results of these trials are set out in Table 1 and in Figures 1-6.

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Fornulation (parts)															
Pionient															1
Hydrocarb 60	100	8	100	90	901	100	100	90	100	90	108	99	190	8	3
Bindor															T
Baystal P 7110 (latex)	12	51	12	23	12	12	12	23	12	27	12	12	2	12	12
															1
rnekener		60	40	0.6											T
CMCFF5		3			0.05	50.6	0.06	0.2	025	0.3	0.35	0.06	90.0	0.25	0.35
Noresin A 180															
Coethy composition data	1						100 Con 100 Co		The state of						
11-11-11-11	69.3	69.2	69.1	69.1	69	692		88.8		693		69	3	2.69	49.1
The source		40	25 05	2.5	8.5	8.5		<b>60</b>		8.5		8.5	8.5	8.5	8.5
H	C	3	3	3	1	L		078	Falsen.	1130		650	435	940	1460
Brookfield viscosity 100rpm (mPa.s)	256	525	20	1310	ğ	3								1	0 ) 0
Caste mecosity 45000 1/8 (mPa.s)	10.2	12.6	16.5	22.6	601			53	187	18.5		11.3	11.5	7.1	41.1
KIDY (afred)	360	285	253	231	360	,		310		269	Jan.	340	360	28	270
AVA (Bur)															
Viscosity data of CMC and Noresin							11.	T. C. C.	J	i i	£!				
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eld viscosity 100pm at 50%	5)	450	, y		9850	423	,				. ,	3120			
(mPa.s)		4624				400									

#### Example 2 - Influence of dry solids on Brookfield viscosity

A number of thickener solutions were prepared as detailed in Table 2. Trials 1 and 1a used the cold water soluble starch ester Noresin A 180. Trials 2 and 2a used cold water soluble native maize starch. Trials 3 and 3a used oxidised cold water soluble starch, Trials 4, 4a, 4.1 and 4.1a used CMC. Trials 5 and 5a used a cold water soluble starch ether and, finally, trial 6 used a cold water soluble hydroxypropylated, nonionic potato starch ether. All of these products, except Noresin A180 and the cws potato starch ether, were provided by Cerestar N.V. The cws potato starch ether was made available from Emsland Stärke GmbH.

The thickener was added to tap water at 40°C in a 2 litre metal beaker and stirred at approximately 3200 rpm for 20 minutes. pH was adjusted to the values shown in Table 2. Brookfield viscosity, Haake viscosity and water retention values (WRVs) were determined using standard methods in the art, both immediately after preparation of the solutions and after overnight storage at 40°C. The results are shown in Table 2 and in Figures 7-10.

It was found that Noresin produced stable viscosities at varying pH and that, at 2.2% dry solids. Noresin produces a Brookfield viscosity which can only be obtained with CMC, for example, at 6% dry solids or with a cold water soluble starch ether at 14.1% dry solids (see Figure 7). It was also observed that the Brookfield viscosity of Noresin solutions remains surprisingly stable during storage, while the viscosity of solutions prepared with cws native maize starch, for example, more than doubles (see Figure 3).

As shown in Figure 9, the Haake viscosity of Noresin solutions was desirably lower than that of solutions prepared with alternative thickeners. Again, the Haake viscosity of Noresin solutions was found to be stable during storage.

Water retention values of Noresin solutions were found to be suitable for use in coating compositions and stable over time (Figure 10). In particular, it was found that the water retention values of Noresin solutions were desirably lower than those of CMC solutions at comparable dry substance.

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Trial		B	1	9	1								
يليزه احترمت حاء وبالمتفرق									-  -				·
Littaener (pare)	8	1001				1	1	1	+	1			
Noresin A 180	1		1	90		   			-		1	+	T
cws native maize starch C+Phis 12015	+	1	3	3	1	2							
01951 still 4 hazzta and - 12910					8	3	+	1		3			
CWS OXIGISED MELZO BILLING							2	8	8	3		1	
CMC FF150	1	T				٠		٠,			8	8	T
cws maine starch ether C'Film 12905	1						T						100
and a start wher Bracol KP 190													
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Solution data					1	. 2. 6.	0.0	2.0	6.0	6.0	14.1	14.1	22
2	2.2	2.2	15.	9.1	33	7:57	Q"		,	9 0	96	9.5	10.7
diy sums	2	4	7.9	95	7.9	9.5	2.7	4.5	0.0	3			900
pH	1		3	9901	1740	1060	153	149	1130.	770	25	1140	2
Brackffeld viscosity 100rpm (mPa.s)	88	55 55	\$		2	1		47	36.1	34.8	49.6	50.2	57.7
Training the defilled 1/3 (mpa.s)	3.7	3.9	-	*,	285	7,87			020	SE SE	270	275	448
Hanke viscousty rooms	328	325	150	H	흥	115			333				
WRV (g/m²)	Ş	54					•						[ ;
Solution data after storage overnight to 40 to 10 thm		7		3	12.7	12.7	2.1	2.1	9	9	14.2	14,2	4.7
50.00	22	77	5	<u> </u>			;	00	8.9	7.9	8.2	5.6	10.5
and some	7.9	9,4	7.4	8.9	7.5	8.7	œ œ	0.0	2		1001	1780	1080
ΡΉ	1	١.	2640	2760	2200	1670	- 47.5	43,5	쭚	929	1	3	
Brookfield viscosity 100rpm (mPa.s)		1	\$		6	2.50	4.7	6.3	35.3	æ	52.4	52.6	57.2
Gaste viscosity 45000 1/s (mPas)	2	\$	1	1	2		1	0003	223	707	264	253	329
	300	216	8	25	8	121	2 1800	2 2000	1				
WKV (g/m²)								•					

Table 2

#### Example 3 - Influence of stirring time on Brookfield viscosity

Noresin and two native maize starch solutions were prepared by adding 2.3% dry substance and 8.9% dry substance, respectively, to tap water at 40°C in a 1 litre metal beaker. The solutions were then mixed at 3200 rpm for 20 minutes. Brookfield viscosity was measured using standard methods. The results are set out in Table 3 and in Figure 11.

	Noresin (2,3% ds)	12015 (8,9% ds)
Time (min)	Brookfield viscosity 10	00rpm/30°C (mPa.s)
5	1100	. 750
10	1040	680
15	1030	720
30	1010	\$80
60	950	1040
120	940	1170
180	930	. 1130
240	940	1210

Table 3

As can be seen from these results, the Brookfield viscosity of Noresin solutions is surprisingly stable compared to that of conventional thickeners.

#### Example 4 - Influence of thickener on torque

Thickener solutions were prepared in 1 litre metal beakers. The thickeners used and the dry solid content of each solution is indicated in Table 4. The solutions were stirred at 1500 rpm until a stable ourve was obtained. Torque was then measured using standard methods with the beginning and end values being recorded. The results are set out in Table 4 and in Figure 12.

It was found that Noresin at low dry substance (2% ds) had similar torque values (i.e. shear resistance) to other thickeners at much higher dry substance. When these more

conventional thickeners are used at low dry substance, it was shown that their water retention values of dropped substantially (CMC is illustrated).

	Noresin (2% ds)	12015 . (9% ds)	12910 (14% ds)	CMC (2% ds)	CMC (6% ds)	12905 (14% ds)
Nm (beginning)	0.015	0.01	0.01	0.014	0.013	0.012
Nm (end)	0.038	0.045	0.042	0.018	0.038	0.042

Table 4

# Example 5 - Influence of dry solids on Brookfield viscosity

Solutions of thickener were prepared as described in Example 2. Brookfield viscosity was measured at several different dry solid contents for each thickener. The results are set out in Table 5 and in Figure 13.

Noresin		160	122	14.4	Section of the section of	TO THE PARTY OF TH
ds (%)	1.5	2,2	3.3		- in the contra near ing	
Brookf (mPas)	590	980	2280	4150	1	
C*Plus 12015				15.		The state of the s
ds (%)	8.6	9	10.2	eparate sharether street		
Brookf (mPa.s)	800	1200	2260		<u> </u>	
C*Plus 12910					140.5	14.3
ds (%)	7.5	9	2 10.3	13.1	13.7	
Brookf (mPa.s)	122	194	290	620	1240	1680
CMC 150			•	* ·	·	and the second second
ds (%)	2	4	6		the state of the state of the state of	
Brookf (mPa.s)	50	250	1100		er et jan jariahalumin kanan	
C*Film 12905	L					The second second second
ds (%)	12.6	13.7	14.9			
Brookf (mPa.s)	550	735	1110	The state of the s		<u> </u>
Emcol KP 190						
	5.2	6.5	. 9.2			***************************************
ds (%) Brookf (mPa.s)	260	406	750	2	de la constitución de la constit	andrew de A

Table 5

These results confirm that high Brookfield viscosities can be obtained with relatively low amounts of Noresin compared to conventional thickeners.

# Example 6 - Assessment of paper quality after coating

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Coating compositions were prepared and applied to paper as shown in Table 6.

Pigments (parts)		
Capim DG	30	
HC 90	70	30
Binder (parts)		70
Acronal S 360 D	12	<del></del>
Chickener (parts)	12	12
CMC FF 10	0.3	
Voresin A-180	V.3	
Additives (parts)		0,25
OBA	0.3	
Inchine parameters	0,1	0,1
lase paper	YWEST	
peed m/min	LWC base	LWC base
Coat weight FS / WS g/m <sup>2</sup>	1800	1800
oating unit	8/8	8/8
coating parameters	FP smooth 12	FP smooth 12
olide%	54.5	1.
H	64.5	64.3
rookfield viscosity mPa.s	8,2	8,3
aaks viscosity mPas	509	300
Ater retention capacity g/m2	13.0	14.8
The state of the s	196	284

Table 6

Printing and gloss were measured using standard methods. The results are shown in Figures 14 and 15, respectively. It was found that Noresin based compositions produced both better smoothness and higher gloss than conventional CMC based coating compositions. In addition, it was found that the use of Noresin instead of CMC did not affect optical properties such as opacity and whiteness.

# THE PATENT OFFICE IN 27 NOV 2003

#### **Claims**

- 1. A paper coating composition comprising one or more thickeners, characterised in that at least one of said one or more thickeners is a cold water soluble starch ester.
- 2. A paper coating composition according to claim 1, characterised in that the cold water soluble starch ester is a starch carbamate phosphate ester.
- 3. A paper coating composition according to claim 1 or claim 2, characterised in that the cold water soluble starch ester is derived from potato or tapicca starch.
- 4. A paper coating composition according to any one of the proceeding claims, characterised in that it comprises 0.005-2% by dry weight, preferably 0.008-1.7% by dry weight of said cold water soluble starch ester.
- 5. A paper coating composition according to any one of the proceeding claims, characterised in that it further comprises one or more pigments, one or more binders and, optionally, one or more additives.
- 6. A paper coating composition according to any one of the proceeding claims, characterised in that it comprises 30-75% by weight dry substance.
- 7. Use of a cold water soluble starch ester in the preparation of a paper coating composition.
- 8. A process for the preparation of a paper coating composition comprising adding one or more pigments, one or more thickeners, one or more binders and, optionally, one or more additives to an aqueous solution and mixing, characterised in that at least one of said one or more thickeners is a cold water soluble starch ester.
- 9. A process according to claim 8 characterised in that the one or more binders are added to the aqueous solution before the one or more thickeners.

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- 10. A process according to either of claim 8 or claim 9 characterised in that, for 100 parts pigment, it comprises 0.01-2 parts cold water soluble starch ester.
- 11. A method of manufacturing paper comprising applying to at least one surface of a sheet of paper or a paper web a composition according to any one of claims 1-6 or prepared according to the process of any one of claims 8 to 10.
- 12. A method according to claim 11, further comprising the steps of removing any excess coating composition, drying and, optionally, calendering the sheet of paper or paper web.
- 13. A paper product coated with a composition according to any one of claims 1-6 or manufactured according to the method of claim 11 or claim 12.

THE PATENT OFFICE III
27 NOV 2003
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#### Abstract

A paper coating composition comprising one or more thickeners, characterised in that at least one of said one or more thickeners is a cold water soluble starch ester, methods of preparing such compositions and their use in coating paper products.

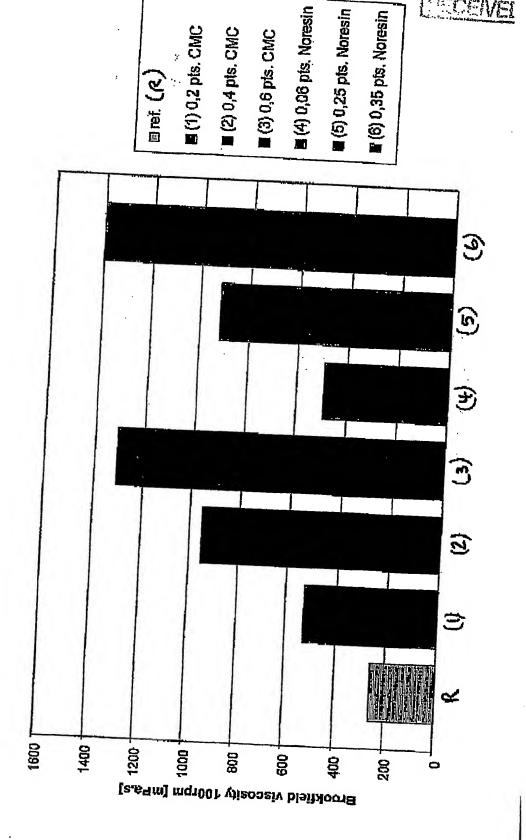


Figure 1

Figure 2

Figure 3

4004

320

300

250

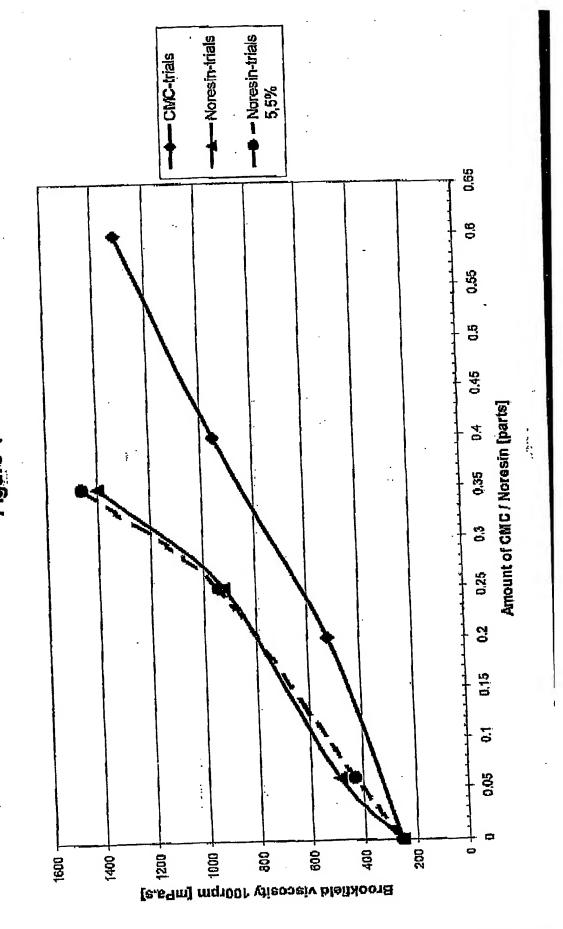
(g/m³) 8 8

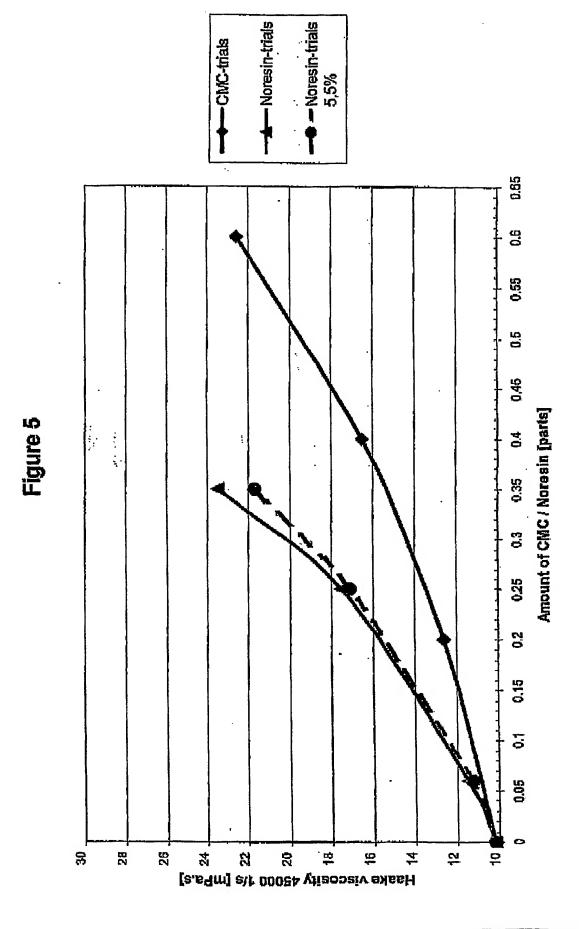
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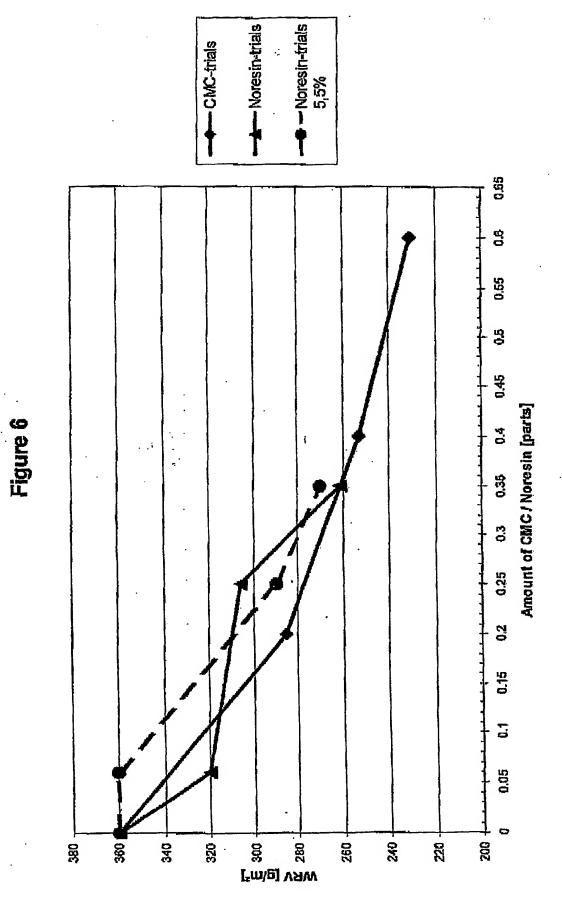
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50

100







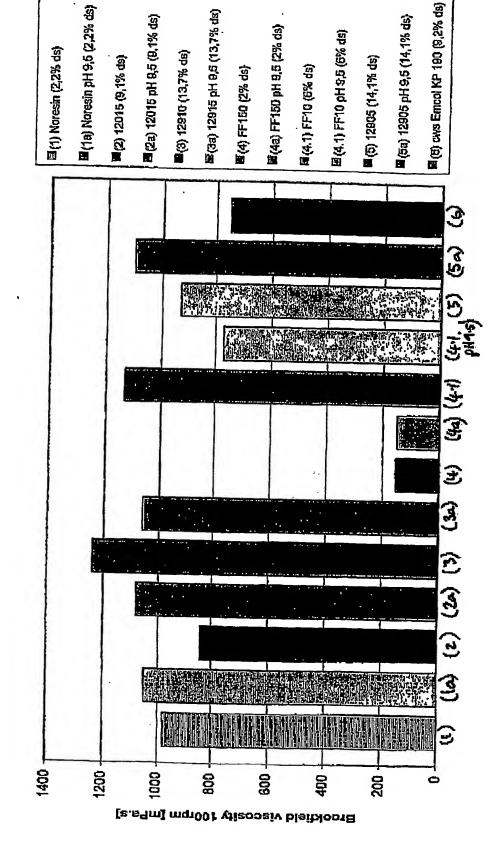
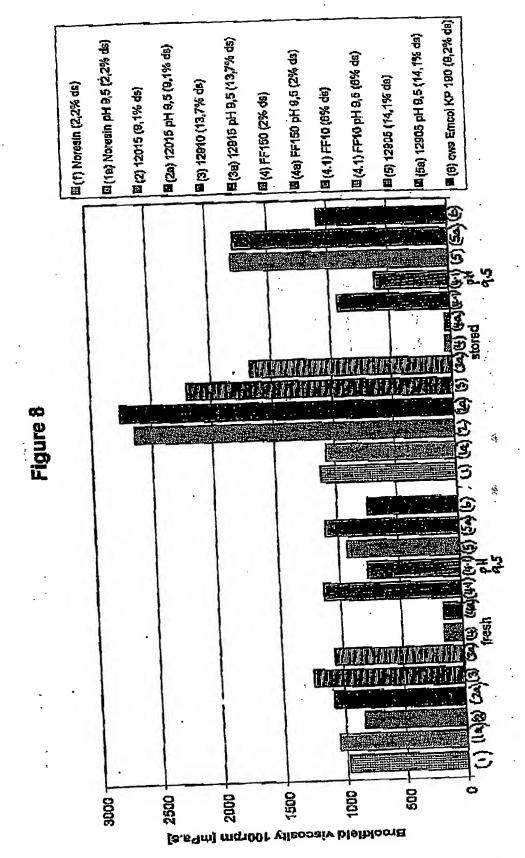


Figure 7

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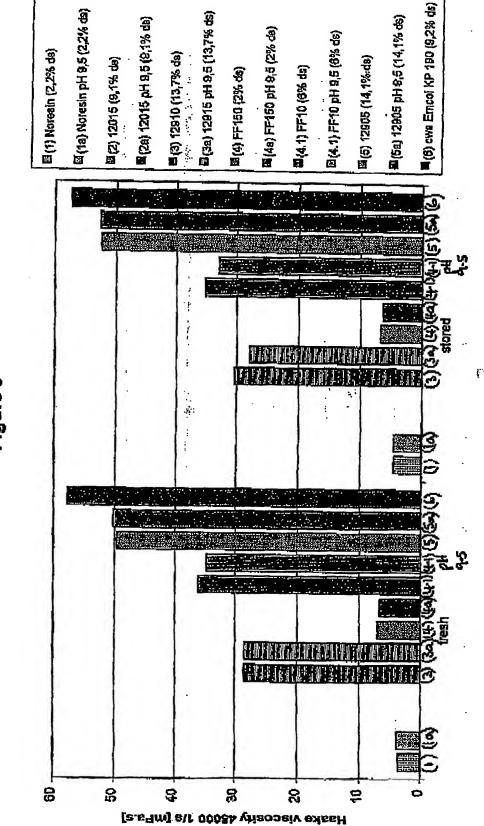
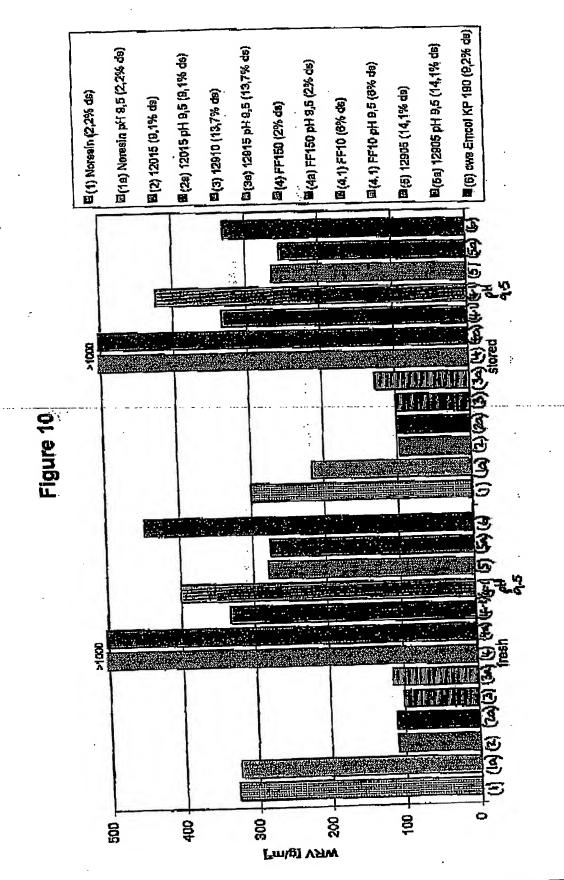


Figure 9

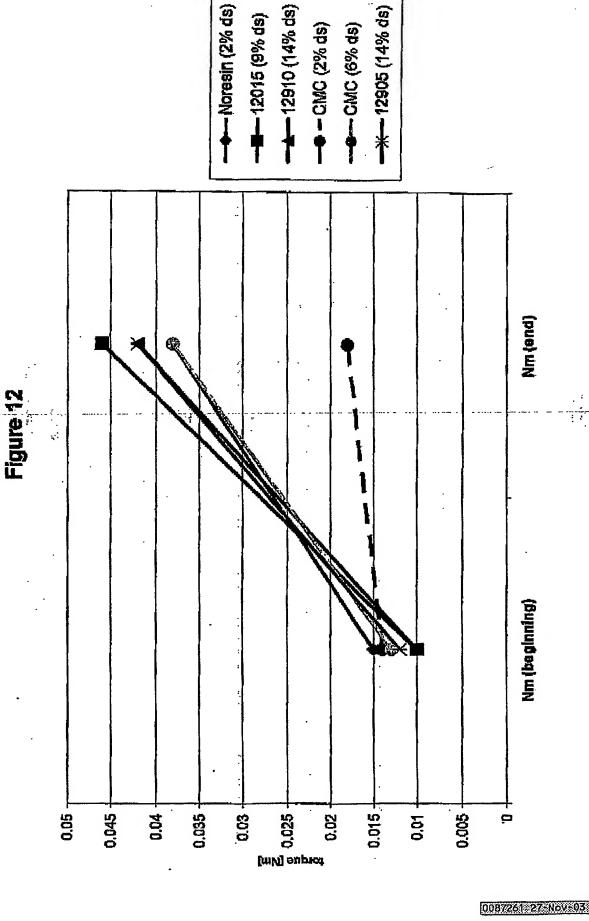
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**36** 240 220 38 -12015 (8,9% ds) 180 <del>1</del>60 140 (Ime (min →-Noresin (2,3% ds) 22 <del>1</del>00 8 8 <del>\$</del> ន 006 Exockfield viscosity 100rpm/30°C [mPa.s] 1400 1300 800

Figure 11

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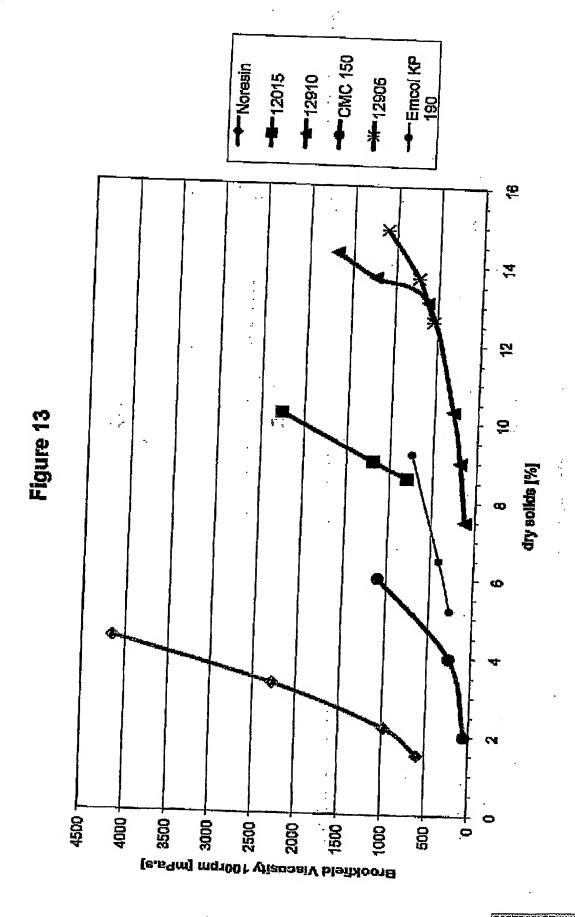


Figure 14

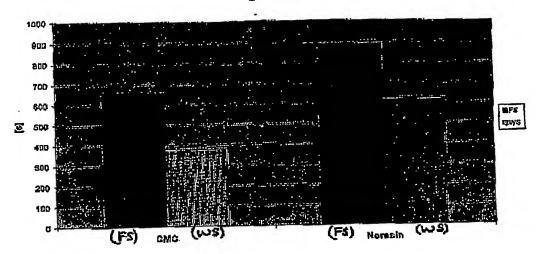
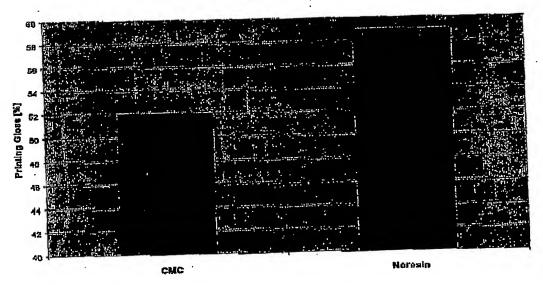


Figure 15



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